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Magnetic properties of quenched Mg-Zn spinel ferrite system

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The study of transition metal oxides particularly spinel ferrite is of great importance from both the fundamental and the applied research points of view. The interesting physical and chemical properties of spinel ferrites arise from the ability of these compounds to distribute the cation among the available tetrahedral and octahedral sites (Blasse 1964). This distribution of cation depends on the method of preparation of samples. The ferrites synthesized by different techniques have been found to exhibit different chemical, structural and magnetic properties (Burriesci *et al* 1978, Kulkarni and Joshi 1986).

In our previous study we have reported magnetic properties of annealed Mg-Zn ferrite system (Kulkarni and Joshi 1985, Joshi *et al* 1985). The aim of the present work is to study the structural and magnetic properties of quenched Mg-Zn ferrite system by means of Mossbauer spectroscopy, X-ray diffraction, low field ac-susceptibility and magnetisation measurements techniques.

Polycrystalline sample of $Zn_xMg_{1-x}Fe_2O_4$ system were prepared by usual ceramic technique. Samples were sintered at 1100°C for 24 hrs and quenched from 1100°C by dropping pellets into ice water. X-ray powder diffraction patterns showed sharp lines corresponding to single phase fcc spinel. The details of the experimental techniques for the measurements of low field ac-susceptibility, saturation magnetisation and Mossbauer are given elsewhere (Joshi 1987).

Lattice constants, a(Å), derived from X-ray diffractograms are shown in Figure 1a for varying Zn concentration, x. The lattice constant increases linearly from $MgFe_2O_4$ to $ZnFe_2O_4$. Therefore it follows Vegards law (Whinfrey *et al* 1960). Increase in a(Å) is because of the fact that the larger Zn^{2+}(0.74 Å) ion replaces the smaller Fe^{3+}(0.60 Å) ion in the spinel lattice.

Results of low field ac-susceptibility are shown in Figure 1b. It is apparent from the Figure 1b that the system exhibits normal ferrimagnetic behaviour. The

Neel temperature determined from the plot shows a sharp decrease with increasing Zn concentration which is due to the decreasing *AB* interactions as Zn replaces Fe from *A*-site.

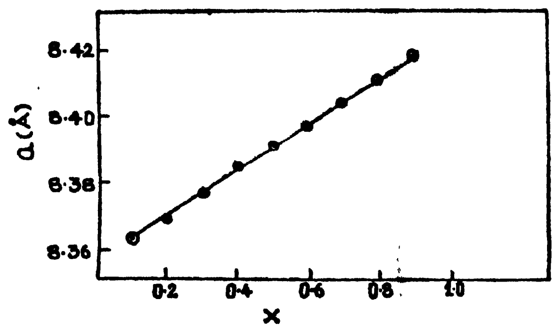

Figure 1(a). Variation of lattice constant, a(Å) with Zn content.

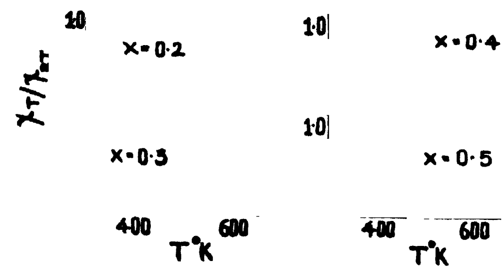

Figure 1(b). χ_T/χ_{RT} as a function of temperature for different Zn concentration.

Figure 2 shows the typical Mossbauer spectra obtained at room temperature (RT). The spectra for $X \leqslant 0.4$ consist of the superposition of two Zeeman sextets due to *A* site and *B* site Fe^{3+} ions. The spectrum for $X = 0.5$ exhibits a relaxation behaviour while for $X \geqslant 0.6$ a paramagnetic quadrupole doublet is observed. The Table 1 gives the parameters derived from Mossbauer spectra.

It is evident from the Table 1 that the isomer shift for *A* and *B* sites show very little change with Zn content which suggests that the *s*-electron charge distribution Fe^{3+} ion is almost uninfluenced by Zn substitution. The observed zero quadrupole splitting for magnetic split sextets indicate co-existence of chemical disorder and overall cubic symmetry in the sample. The quadrupole splitting for $X \geqslant 0.6$ at the *B* site decreases monotonically with X which is attributed to an increase in the oxygen parameter with Zn concentration.

The variation of hyperfine field for *A* and *B* sites as a function of *X* is shown in Figure 3a for $X \leqslant 0.4$. Similar variations in H_A and H_B were also observed for other zinc substituted ferrites (Daniels and Rosenewaig 1970, Leung *et al* 1973, Petitt and Forester 1971 and Kulkarni and Joshi 1985). This variation can be explained on the basis of the canting of the spin on the *B* site as Zn occupies *A* site.

In order to understand the variation of hyperfine field magnetisation measurements were carried out for $X \leqslant 0.9$ at RT. The saturation magnetisation of all

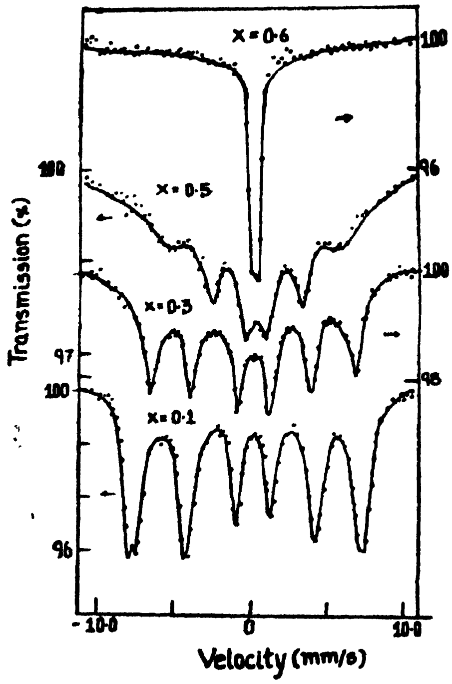

Figure 2. Typical room temperature Mossbauer spectra for Mg-Zn ferrite system.

the samples have been estimated within the accuracy of 5%. The magnetic moment per formula unit, n_B, is seen to be maximum when X lies between 0.4 and 0.5.

Table I. The Mossbauer parameters isomer shift (IS)* and quadrupole splitting (QS) at RT for $Zn_xMg_{1-x}Fe_2O_4$ system.

X	IS (mm/sec)		QS (mm/sec)	
	IS(B)	IS(A)	QS(B)	QS(A)
0.1	0.34 ± 0.02	0.28 ± 0.02	0.00 ± 0.02	0.00 ± 0.02
0.2	0.31 ± 0.02	0.25 ± 0.02	0.00 ± 0.02	0.00 ± 0.00
0.3	0.33 ± 0.02	0.29 ± 0.02	0.00 ± 0.02	0.00 ± 0.02
0.4	0.34 ± 0.02	0.27 ± 0.02	0.00 ± 0.02	0.00 ± 0.02
0.5	Relaxation spectrum			
0.6	0.29 ± 0.02	—	0.58 ± 0.02	—
0.7	0.26 ± 0.02	—	0.55 ± 0.02	—
0.8	0.27 ± 0.02	—	0.49 ± 0.02	—
0.9	0.30 ± 0.02	—	0.43 ± 0.02	—

*With respect to iron metal.

The observed n_B dependence on X is a common feature for the mixed ferrite systems (Daniels and Rosenswaig 1970, Leung *et al* 1973, Srivastava *et al* 1979, Kulkarni and Joshi 1985).[1] Adopting the procedure of Daniels and Rosenewaig (1970), values of relative magnetisation as a function of X were determined using the observed values of hyperfine field and distribution of Fe ions on A and B sites. This result

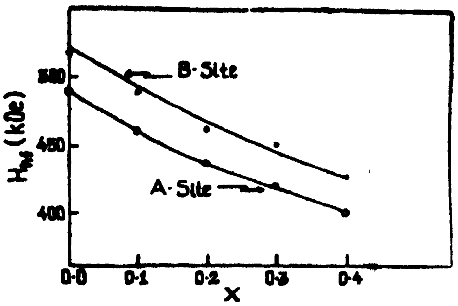

Figure 3(a). Variation of nuclear hyperfine field with Zn content.

is compared with the value obtained from magnetisation measurements. It is clear from the Figure 3b that there is an agreement for $X \sim 0.1$ but becomes increasingly worse as Zn content increases. This behaviour indicates the existence

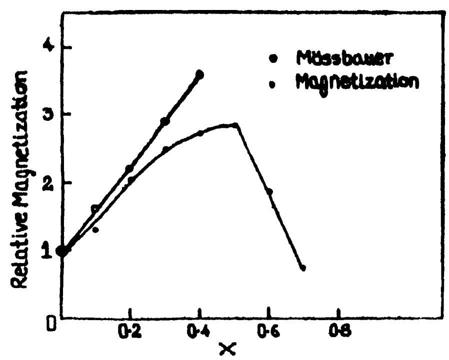

Figure 3(b). Relative magnetization vs X for Mg-Zn ferrite system.

of canted spin structure for $X \geqslant 0.1$ because the Mossbauer effect measures the magnitude of $\langle S_z \rangle$ while the macroscopic magnetisation measurement depends on the component of $\langle S_z \rangle$ parallel to the external field.

According to Petitt and Forester (1971) there is generally a distribution in the B site canting angle because of the presence of distribution in nearest neighbour magnetic environment of a given B site cation. Therefore writing average B site canting angle as $\bar{\theta}_B$ the magnetic moment per formula unit is given by

$$n_B = \mu(Fe^{3+})(1+X) \cos \bar{\theta}_B - \mu(Fe^{3+})(1-X) \tag{1}$$

Considering the values of n_B, $\bar{\theta}_B$ has been calculated using eq. (1) for different values of X and it was found to vary between 26° to 76° for $X=0.2$ to $X=0.7$. These results are consistent with those from earlier studies in spinels (Bhargava and Ze 1980, Hubsch and Gavoille 1982, Petitt and Forester 1971). Since (Rosenewaig 1970a,b, Patton and Liu 1983)

$$\cos \bar{\theta}_B \propto \frac{Z_{AB} J_{AB}}{Z_{BB} J_{BB}} \tag{2}$$

the increase in $\bar{\theta}_B$ with X is due to the decrease in Z_{AB}, the average number of A site magnetic nearest neighbour to a B site cation, when Zn is introduced in the lattice. Therefore, the observed decrease in H_A and H_B is due to the decrease in the AB interaction and it could also be attributed to the fact that Neel temperature decreases sharply with Zn substitution.

Results of variation of hyperfine field, Neel temperature with Zn concentration and the presence of canting from $X \geqslant 0.1$ indicate that because of quenching, there is appreciable change in magnetic AB interaction compared to that in annealed sample.

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